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LLNL-PROC-415740

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August 18, 2009

APS Shock Compression of Condensed Matter
Nashville, TN, United States
June 28, 2009 through July 3, 2009

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THERMAL DAMAGE CHARACTERIZATION OF ENERGETIC MATERIALS

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Abstract. We conducted thermal damage experiments at 180˚C on PBXN-9 and characterized its material properties. Volume expansion at high temperatures was very significant which led to a reduction in material density. 2.6% of weight loss was observed, which was higher than other HMX-based formulations. Porosity of PBXN-9 increased to 16% after thermal exposure. Small-scale safety tests (impact, friction, and spark) showed no significant sensitization when the damaged samples were tested at room temperature. Gas permeation measurements showed that gas permeability in damaged materials was several orders of magnitude higher than that in pristine materials. In-situ measurements of gas permeability and density were proved to be possible at higher temperatures.

INTRODUCTION

Thermal incidents such as fires in storage bunkers, magazines, and transportation carriers (trucks, aircrafts, ships) would expose energetic materials to unexpected heat that may damage the explosive charge. Thermal damage could change the material composition, introduce voids, increase porosity, and alter sample dimension. Effect of thermal damage and mechanical damage have been previously reported by Hsu et. al (1-5). Gas permeability and burn rates in thermally-damaged LX-04 and LX-10 increased by several orders of magnitude (2) due to higher and lower density. Detonation velocity and detonation energy density of LX-04 and LX-17 were significantly lowered upon thermal exposures (3,4). Some damaged materials, either through aging or thermal exposure became weaker mechanically and easily to break apart. Vandersall et. al reported that heated energetic materials were more sensitive to shock initiation at high temperatures (5). PBXN-9 is an HMX-based plastic-bonded explosive, which consists of 92 wt.% HMX, 6 wt.% of % dioctyl adipate (DOA), 2 wt% carboxyl-terminated polybutadiene (HYTEMP 4544). Ignition kinetics and burn rates of PBXN-9 were recently studied and reported (6). In this paper, we will describe our experimental approach and results in conducting thermal damage experiments on PBXN-9, measuring gas permeability, porosity, and sample volume.

EXPERIMENTAL TECHNIQUES

1. Un-confined thermal damage experiment

Process parameters for thermal experiments (heating temperature and heating durations) can be estimated from ODTX (one dimensional time to explosion) data. The ODTX system at the Lawrence Livermore National Laboratory can precisely measure times to explosion and minimum ignition temperatures of energetic materials. These measurements provide insight into the relative ease of thermal ignition and

allow for the determination of kinetic parameters (7). Table 1 lists times to explosion data for LX-04, LX-10, LX-17, and PBXN-9. It shows that PBXN-9 can be heated at 181˚C for ≤ 7 hours without thermal ignition (6).

TABLE 1. ODTX data

Samples	ODTX, hours
LX-04	@< 183 C, >20 hours
	@ 183 C, 20 hours
	@192 C, 6.6 hours
	@199 C, 3.6 hours
LX-10	@200 C, 1.1 hours
	@195 C, 4.4 hours
	@190 C, 6.1 hours
	@181 C, > 28 hours
LX-17	@ 268 C, 1.9 hours
	@ 259 C, 2.9 hours
	@250 C, 7.2 hours
	@ 240 C, > 28 hours
PBXN-9	@192 C, 1.6 hours
	@181 C, 7.0 hours
	@171 C, 15.4 hours
	@166 C, >138 hours

Thermal damage experiments were first conducted in a portable oven in an un-confined condition at 180˚C inside a 1.0-kg shot tank for 3 hours. The specimens were allowed to expand during the thermal experiment without restraint to simulate fire incidents of explosive charges stored in unconfined environments. They were subsequently characterized for small-scale safety, volume, density, and gas permeability at ambient condition.

2. Thermal experiment of partially-confined samples

Gas permeability data are important in modeling the performance of explosives. The gas permeation system at LLNL can measure the gas permeability from ambient temperature to 250˚C, vacuum to 3 x 10^5 Pa with a detection range of 10^{-12} to 10^{-20} m^2. The specimen was glued to a sample holder which provided a radial confinement. The specimen can also be fully confined with porous plates on the top and the bottom of the specimen. Detailed description of gas permeation systems can be found elsewhere (1,2,8,9).

We also conducted thermal damage in-situ in the gas permeation system. The gas permeability of pristine sample was measured at ambient temperature, followed by heating the sample at 1.2 ˚C/min to 150˚C, soaked for 75 minutes, measured gas permeability in-situ; ramped up to 180˚C, soaked for 75 minutes, and measured the gas permeability.

RESULTS AND DISCUSSIONS

1. Results of dimensional characterization and safety testing

Small-scale testing (drop hammer, spark, and friction) was performed on damaged PBXN-9 samples which were heated to 180˚C and cooled to room temperature. The results are shown in Table 2 along with dimensional measurements. Sample expanded by 13%, from 1.09 cm^3 to 1.23 cm^3. This was similar to other HMX-based formulations (2,3). Weight loss was 2.6% that was higher than those from LX-04 and LX-10, probably due to the evaporation and/or decomposition of DOA. This was confirmed by the result of thermogravimetric analysis (TGA) of DOA/binder. TGA result showed 50% wt losses under the same thermal damage conditions. Small-scale safety testing showed no apparent changes in impact, friction and spark sensitivities for thermally damaged PBXN-9 when tested at room temperature.

TABLE 2. Dimensional measurement and small scale test results on heated and then cooled PBXN-9 samples

Test	Ambient PBXN-9	180˚C for 3 hours
Weight Loss %	0	-2.63
Bulk volume (cm^3)	1.09	1.23
Drop Hammer (cm)	68	60
Friction	0/10@ 36 kg	1/10@ 36 kg
Spark	0/10 @1.0 J	0/10 @1.0 J

2. Density and porosity of damaged PBXN-9 measured at ambient temperature

PBXN-9 specimens, after thermal exposure and cooled, were characterized with a pycnometer for density and porosity at ambient temperature. The density obtained from the gas pycnometer is often called true density in that it is very close to theoretical maximum density (TMD) of the material if fraction of closed pores in the sample is insignificant. Porosity calculation from the pycnometer measurement was described elsewhere (2). Upon thermal exposure, pores, cracks, gaps formed, as shown in Figure 1. Table 3 lists the density and porosity of PBXN-9 measured at ambient temperature. It shows that the total porosity of damaged sample increased from 2.4% to 15.5%. Most of pores and voids were open pores which would contribute to gas flow in the material and would lead to faster burn rates and higher gas permeability.

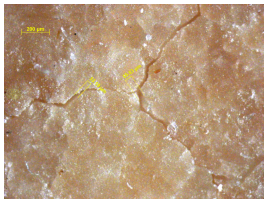

FIGURE 1. Damaged PBXN-9 pressed part showed cracks/gaps (50 microns wide).

TABLE 3. Density and porosity, fraction of closed pores, fraction of open pores of PBXN-9 samples; before and after thermal damage; ρ_b =bulk density; ρ_t = true density; ε = total porosity; f_o = fraction of open pores.

Sample	ρ_b, g/cc	ρ_t, g/cc	ε, %	f_o,%
Pristine	1.741, 97.64% TMD	1.777, 99.64% TMD	2.36	2.00
Damaged,	1.505, 84.47% TMD	1.754 98.36% TMD	15.53	13.89
% Change	-13.17	- 1.26	13.17	11.89

3. Gas permeability measurements at ambient temperature and high temperature

Gas permeation in explosives is highly dependent of density, particle size, and porosity. Gas permeability was made at room temperature on pristine and thermally damaged PBXN-9. Table 4 shows results of the measurements on pristine samples of various densities and damaged samples. The gas permeability in the high density pristine PBXN-9 (97.7% TMD) was below the detection limit of the system (10^{-20} m^2). Gas permeabilities in pristine samples increased by 6 orders of magnitude as density decreases from 97.7% TMD to 89.3% TMD. Thermal exposure induces voids, reduces density, and increases gas permeability by several orders of magnitude, depending heating temperature, duration, and confinement. Thermally damaged PBXN-9 showed a gas permeability of 6.5 x 10^{-13} m^2 after thermal exposure. We are in the process of measuring gas permeability in-situ for several HMX-based formulations. Pristine part was potted to the holder, measured, followed by heating to a pre-determined temperature at a certain ramp rate, soaked, and measured. Figure 2 shows the results of the in-situ measurements made on PBXN-9. By this approach, it is

possible to estimate sample bulk density (real-time) during thermal insults. We plan to use the methodology to obtain gas permeability and density data for other high explosive formulations in various confinements and temperature profiles. Data modeling is underway and will be reported in a later date

TABLE 4. Gas permeability measurements on PBXN-9 at room temperature.

Sample description	Density, g/cc	Gas Permeability m^2
Pristine	97.7% TMD	$< 10^{-20}$
Pristine	95.3% TMD	1.7×10^{-16}
Pristine	92.0% TMD	3.7×10^{-15}
Pristine	89.3% TMD	2.6×10^{-14}
Damaged*	< 89.3% TMD	6.5×10^{-13}

* The damaged sample was from a 97.7% TMD pristine part, which was thermally damaged, and then potted after it was cooled to room temperature.

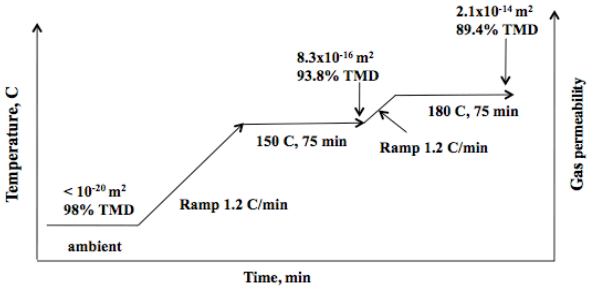

FIGURE 2. Gas permeability and bulk density at various temperatures for the radially-confined PBXN-9 specimen.

ACKNOWLEDGEMENTS

The authors would like to thank: Sally Weber for preparing the pressed parts for the small scale tests; Gary Hust and Heidi Turner for conducting small-scale safety tests and TGA measurements. In addition, useful discussions with Dr. William Chew of U.S. Army is highly appreciated. PBXN-9 material was provided by AMRDEC of the US Army. This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

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